



The Effect of nitric oxide on the photocatalytic oxidation of small hydrocarbons over titania

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ABSTRACT

The catalytic UV photo-oxidation of NO in the absence and presence of ethane, ethene, propane, propene, and *n*-butane over TiO₂ in the presence of excess oxygen was studied in the temperature range 21–150 °C. It was confirmed in our system that in the absence of hydrocarbon NO was photocatalytically oxidised by oxygen to NO₂ over TiO₂ and was strongly absorbed. Both NO and hydrocarbon could be simultaneously photo-converted with the conversion varying considerably with both NO and hydrocarbon concentration and the nature of the hydrocarbon. In some instances the presence of NO in the feed gas enhanced hydrocarbon oxidation via reactions involving NO₂ that is a powerful oxidant. The extent of this effect depended on the relative strengths of adsorption on TiO₂ of the reactants and products. To reduce surface coverage of hydrocarbon most reactions were run at 150 °C, and it was shown that at this temperature NO_x adsorbed on titania could be reduced by photogenerated hydrocarbon surface species to N₂O and N₂ under these conditions. The formation of N₂ was confirmed using ¹⁵NO with helium as carrier gas. By contrast, at room temperature in the presence of propene NO was converted to NO₂.

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1. Introduction

Previously we studied the catalytic photo-oxidation of ethane, ethene, propane and propene over titania, in excess oxygen and found under most conditions at room temperature the selectivity of hydrocarbon conversion to CO₂ was at least 95%. We also studied reactions with *n*-butane and *n*-hexane, and they had significantly lower conversion to CO₂. The reasons for this were not explored, but the formation of brown carbonaceous surface deposits on the titania were implicated [1]. There is a lot of interest in the photo-oxidation of NO to NO₂ in the presence of oxygen, and eventually to nitric acid if sufficient adsorbed water is present [2–12], and TiO₂ is being used on building materials for the removal of atmospheric pollutants in urban areas via these reactions. Although some suggest the oxidative cleansing action involves the formation of nitric acid, it seems equally likely the extremely powerful oxidant NO₂ is directly involved. A number of studies have also dealt with the photodecomposition and photoadsorption of NO with titania surfaces [13–17] in the absence of oxygen which seems to be a

complex reaction since different workers reported widely varying products including NO₂, N₂O, and NO^{3–}.

NO₂ is a very powerful oxidant, and it has long been known it reacts rapidly with hydrocarbons in the gas phase [18], that it can oxidise soot from diesel engines at moderate temperatures [19] and that NO₂/hydrocarbon mixtures can form the basis of rocket propellant systems. We therefore thought it worthwhile to explore the effect of NO on the photo-oxidation of hydrocarbons over titania, since NO₂ should be generated *in situ* on the titania surface so keeping it free of carbonaceous deposits. A number of papers have been published on photoinduced reactions of NO and hydrocarbons over titania [20–22], in addition two recent studies dealt with the photoreaction of NO with CO [23] and NH₃ [24] over titania.

Here we report results for the catalytic oxidation of ethene, ethane, propene, propane, and *n*-butane in the presence of NO and excess oxygen, and surprising evidence was obtained showing photogenerated surface organic fragments can reduce nitrogen oxide species to dinitrogen. Outside the field of photocatalysis the hydrocarbon selective reduction of NO (HC-SCR) in the presence of excess oxygen has attracted great interest, and the subject has been extensively reviewed [25–30]. The most effective catalysts are Pt/alumina, Cu exchanged ZSM5 and Ag/alumina though a large

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variety of other Cu, zeolite and pgm based systems have also been studied. Interestingly the mechanism of NO reduction via HC-SCR often invokes the formation of NO_2 which subsequently reacts with an activated hydrocarbon species.

2. Experimental

The photo reactor comprised a stainless steel Plate 100 mm \times 100 mm evenly coated with TiO_2 by spraying its upper surface with an emulsion of TiO_2 in water, followed by drying at room temperature. Reactant gas mixtures were passed over the TiO_2 through a 1 mm wide gap between a quartz window and the sample plate. A viton gasket made a gas tight seal between the quartz plate and a stainless steel block which contained a recess that retained the sample plate, as illustrated in Fig. 1. The whole assembly holder could be heated to temperatures up to 150 °C by a hotplate on which the stainless steel block was placed. An air-cooled housing containing a broad-spectrum 400 W lamp (Philips HPA 400 S) was placed 50 mm above the centre of the sample plate. The lamp reached full intensity within three minutes. The full output was 66.8 mW/m² with visible and UV accounting for 43.2% and 56.8% of the output respectively. The output in the UV region consisted of 49.3% in the UVA and 8.8% in the UVB and C regions [31]. With the sample at 150 °C there was an increase of \sim 3 °C when the light was switched on. After \sim 30 min the sample temperature returned to 150 °C as the feedback gas temperature controller reduced the input power to compensate for the heating effect of the lamp. Unless otherwise stated experiments were carried out at 150 °C and 250 ml/min total gas flow rate with varying concentrations of hydrocarbon and NO while maintaining an O_2 concentration of 12%. Gases were obtained from bottles (Air Products), and mass flow controllers were used to produce desired mixtures and flow rates.

Reactor outlet gas was analysed using a quadrupole mass spectrometer (VG Gaslab 300) and for N_2O and C_2H_6 a GC (PerkinElmer 8500) was used. When no NO was present in the gas feed the C_2H_6 conversion was determined from the change in the mass 30 signal monitored by the mass spectrometer. However, when NO (also mass 30) was present in the gas feed the C_2H_6 conversion was determined with the GC. Once the C_2H_6 conversion was known from the GC its contribution to the mass 30 signal could be calculated, and so the amount of NO from the mass 30 signal obtained. The C_2H_6 conversions in the absence of NO in the gas feed calculated using the GC and mass spectrometer data agreed to within $\pm 5\%$. Contributions to the mass 30 signal (used to monitor NO) arise from the fragmentation of NO_2 which unambiguously also gives a mass 46 signal. This fragmentation was determined using a known NO_2 concentration and then used to compensate for NO_2 in the mass 30 signal.

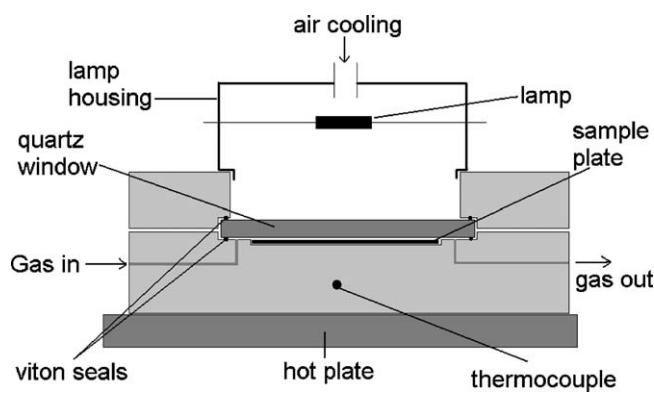


Fig. 1. Schematic of photoreactor.

In all of the experiments described here the TiO_2 used was "Hombifine N" obtained from Sachtleben Chemie GmbH, Germany. Anatase was the only crystalline phase identified by X-ray diffraction (Siemens D500 Diffractometer) with an estimated crystallite size of 6.8 nm from line broadening. The BET surface area was 357 m² g⁻¹. Typical TiO_2 loadings on the sample plate were between 0.3 g and 0.4 g, and from this a TiO_2 film thickness of 7.5–10 μm was estimated assuming a density of 3.89 g cm⁻³ (i.e., 100% packing efficiency). In practice the film was somewhat thicker than this due to inefficient packing. The typical penetration depth of UV light into powdered TiO_2 is about 2 μm , and twice this thickness of film would be required for saturation of the reaction rate. Consistent with this only small changes ($\pm 5\%$) in propene conversion were observed when the TiO_2 loading was varied between 0.16 g and 1.28 g, corresponding to a film thickness of 4 μm and 32 μm respectively (assuming 100% packing efficiency).

3. Results and discussion

3.1. Hydrocarbon oxidation in the absence of NO

Previously we reported results for the UV-induced photo-oxidation of propene, propane, ethene, ethane, *n*-butane and *n*-hexane over a TiO_2 photocatalyst at 150 °C with hydrocarbon concentrations up to 4000 ppm and O_2 concentrations up to 20% [1]. In the absence of O_2 , a small amount of reaction was observed for just a short period. Increasing the O_2 concentration led to increased hydrocarbon conversion. With hydrocarbon concentrations up to \sim 1000 ppm conversion to CO_2 was at least 95% for propene, propane, ethene and ethane though the CO_2 selectivity fell at higher concentrations and at all *n*-hexane concentrations down to 50 ppm there was little reaction.

For propene and propane, we previously showed the extent of photoconversion depended on the gas-phase hydrocarbon concentration, and had maxima at 500 ppm and 1000 ppm, respectively. The decrease at higher concentrations was attributed to hydrocarbon blocking oxygen adsorption sites, and thereby inhibiting the production of the photogenerated reactive oxygen species responsible for hydrocarbon oxidation. This effect also explains the increased conversion of hydrocarbon at 150 °C compared to that at room temperature observed for propene. The increased temperature reduces the amount of adsorbed propene and allows more reactive oxygen species to be generated. It was for this reason that most experiments reported (here and those done previously) were carried out at 150 °C, so higher NO and hydrocarbon conversions could be achieved. Increased photo-oxidation at slightly elevated temperature due to the lowering of a hydrocarbon blocking effect has also been reported for other related systems [32,33]. Durability of the photo-oxidation reaction without catalyst deactivation was demonstrated for propene, propane, ethene and ethane. In contrast with *n*-butane and to a greater extent *n*-hexane, the deposition of carbonaceous species on the TiO_2 surface led to rapid catalyst deactivation.

It was thought the presence of photogenerated NO_2 might keep the surface clean and so improve conversions by oxidizing them to CO_2 and H_2O , and re-forming NO. Therefore the current paper focuses on the effect of NO and hydrocarbon which is reported in the following sections.

3.2. Photo-oxidation of NO to NO_2

Initially experiments were made on the photo-oxidation of NO to NO_2 in the absence of hydrocarbon, and the results using varying NO concentrations in an excess of oxygen are given in

Table 1

Photoinduced NO conversion for gas mixtures containing NO (various concentrations), O₂ (12%) and He (balance) at 150 °C and a total flow rate of 250 ml/min.

NO concentration (ppm)	NO conversion (%)	NO conversion (ppm)
2000	4	80
580	12	70
300	29	87
152	78	119
76	80	61

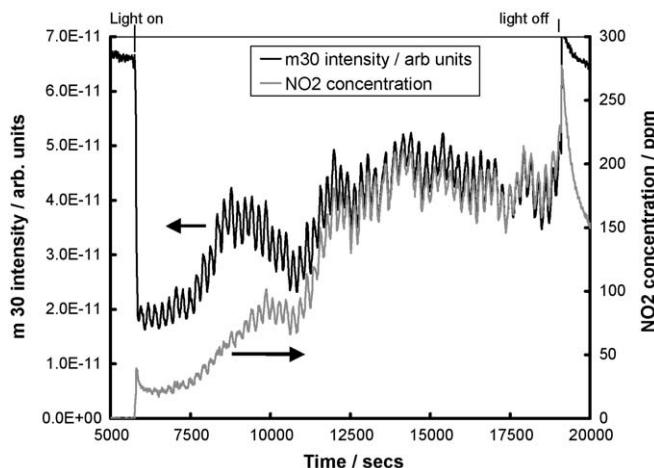


Fig. 2. Photoconversion of NO to NO₂ over Hombifine N TiO₂ with 300 ppm NO, 24% O₂ balance with a flow rate of 250 ml/min at 150 °C. Note that NO₂ (mass 46) gives a strong contribution to the mass 30 signal in addition to that from NO so the mass 30 signal rises from ~7500 s in line with the increase in NO₂. The final NO conversion, at 64%, was calculated using a correction factor to the 30 signal derived from a known concentration of NO₂.

Table 1 and **Fig. 2**. From gas phase analyses NO₂ appeared to be the only product (with no N₂O detected), although its concentration in the gas exiting the reactor took several hours to increase to a steady limiting value. When this limiting value was reached the nitrogen balance was within 10% for NO being converted exclusively to NO₂. This gradual rise of the measured NO₂ was presumably due to strong adsorption of the NO₂ as it was formed on the titania surface and can be accounted for by the formation of ~0.1 of a monolayer of NO₂ (assuming 1 monolayer is 5×10^{14} sites/cm²). The percentage conversion of NO to NO₂ decreased with increasing inlet NO concentration, although the absolute amount of NO converted remained fairly constant over the concentration range of 76–2000 ppm. This probably results from NO conversion being limited by O₂ activation rather than NO adsorption and in keeping with this (with 300 ppm NO) the NO conversion was increased by increasing the O₂ concentration—NO conversions of 59% and 83% were obtained with 20% and 40% O₂ respectively.

3.3. Effect of temperature on the photoreaction of NO and propene in the presence of O₂

Most experiments in this paper were performed at 150 °C, but initially we carried out some experiments at lower temperature. The first experiments were carried out with 300 ppm propene and 300 ppm NO with the reactor heater switched off, and the temperature was gradually ramped to 150 °C. After a short period when some NO/propene adsorption was observed no reaction was observed at room temperature with the light off. With the heater switched off light exposure caused a gradual increase in the sample temperature from 22 °C to 43 °C over 30 min. Mass spectrometer

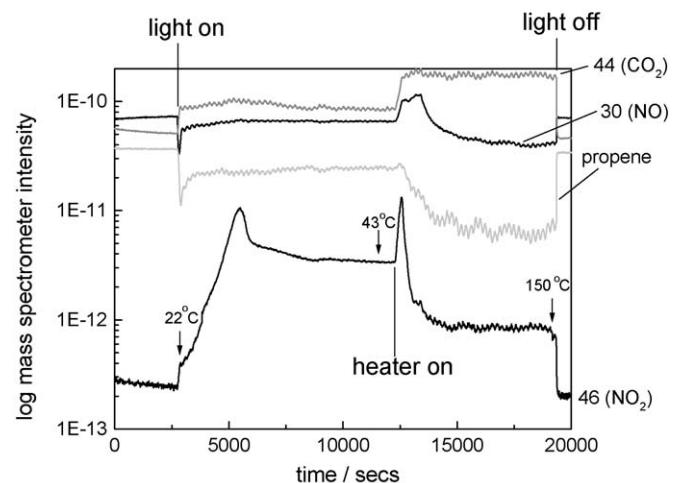


Fig. 3. Mass spectrometer intensities as a function of time for the photocatalytic conversion of NO and propene. Masses monitored (and chemical assignment) given in labels on right of graph. Gas feed: 300 ppm propene, 300 ppm NO, 12% O₂ balance He. Temperatures as indicated, 250 ml/min total flow rate. Catalyst: Hombifine N TiO₂.

intensities monitored during this experiment are shown in **Fig. 3**. From the results it is clear that both propene and NO reacted on light exposure, with the products of the reaction being water, CO₂ and NO₂. The maximum CO₂ intensity was reached very quickly though there was a more gradual rise in the NO₂ signal which reached a steady value after about 30 min at which point the sample temperature had stabilised at ~43 °C. Then the selectivity of NO and propene conversion to NO₂ and CO₂ was 100% with conversions of 36% and 31% respectively. In this and other experiments the conversions were stable over several hours after an initial stabilisation period. The initial gradual rise in the NO₂ intensity may be caused by the adsorption of NO₂ on the TiO₂, with the gas phase NO₂ increasing in concentration after the surface is saturated. This gradual rise in NO₂ was also observed for NO photo-oxidation in the absence of hydrocarbon.

On heating the reactor to 150 °C there was a significant increase in propene and NO conversion to 82% and 63% respectively together with a corresponding rise in the CO₂ intensity. There was however, a decrease in the NO₂ intensity suggesting a switch in selectivity from NO oxidation to NO reduction. This is unusual for as described above most authors report NO photo-oxidation to NO₂ in the presence of oxygen. Clearly in the presence of hydrocarbon the situation is different and suggests NO₂ reacts with hydrocarbon species (though only at slightly elevated temperature) leading to reduction of the NO₂ back to NO and some conversions to N₂ and N₂O. The reaction of NO₂ with hydrocarbon species is also consistent with results described above in which higher selectivity to CO₂ was observed at higher hydrocarbon concentrations in the presence of NO than in the absence of NO. When the light was switched off all four of the signals monitored in **Fig. 3** returned to their original intensities before illumination showing no significant thermal reaction occurred at 150 °C.

3.4. Effect of NO/hydrocarbon ratio and concentration

3.4.1. NO/propene

The conversion of NO and propene as a function of propene concentration in the gas feed both without NO and at a constant NO concentration of 300 ppm are shown in **Fig. 4** and **Table 2**. At propene concentrations up to 300 ppm, conversion of propene was essentially complete. For concentrations above 580 ppm not only did the percentage conversion decrease but also the absolute

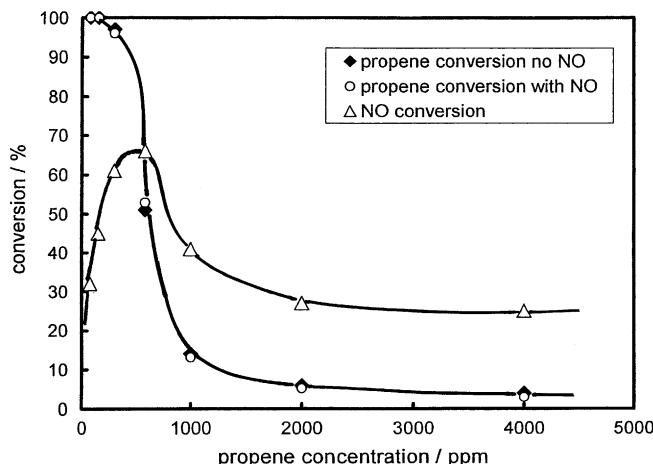


Fig. 4. Conversion of NO and propene as a function of propene concentration in the absence of NO and with 300 ppm NO in the gas feed.

amount. At higher propene partial pressures the photocatalytic activity was inhibited. A possible explanation for this is high surface propene concentration prevents oxygen from reaching the surface and participating in propene combustion. Indeed a similar poisoning effect was observed for propene in the absence of NO. So it is not surprising NO had little effect on the propene conversion. In addition the NO conversion clearly followed that for propene, it is therefore the oxidation of the propene that produces the conditions for NO conversion. The exact mechanism of this process is unclear, but it could involve surface reactions between NO and species formed during the partial oxidation of propene.

Fig. 5 summarises the NO and propene conversion with constant (300 ppm) propene concentration and varying NO concentration. Increasing NO concentration to 580 ppm the absolute NO conversion increased while the propene conversion remained essentially complete. For NO concentrations of 1000 ppm and 2000 ppm the propene conversion was inhibited falling to 62–64% and there was a decrease in the NO conversion compared with 580 ppm NO. The fall in propene conversion at high NO concentrations may again be an inhibition effect on either propene or oxygen adsorption by NO.

Experiments were also carried out with a constant NO to propene ratio, but varying absolute concentration. The results are also summarised in Table 2 which also shows some speciation of the NO products. It is interesting to note that even for NO to propene ratios of 6.7–1 very little NO₂ was generated unless the

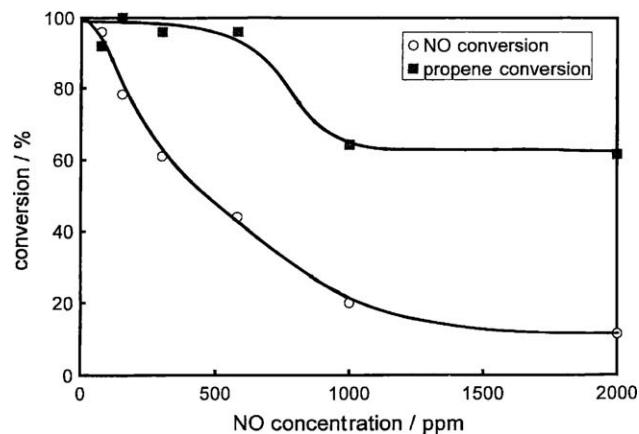


Fig. 5. Conversion of NO and propene as a function of NO concentration with 300 ppm propene in the gas feed.

propene concentration was below 300 ppm. The significant factor in determining NO conversion to NO₂ in these experiments therefore seems to be the O₂ to propene ratio. Mechanistically this may be due to the hydrocarbon species preferentially reacting with active surface oxygen species during the photocatalytic reaction and it is only when the hydrocarbon concentration falls to a low enough level that some oxygen species are able to react with NO. Also shown in Table 2 are some selected measurements for the N₂O production (using GC analysis). For the range of conditions examined the N₂O yield varied between 25% and 36%. At 21–41 °C, with 8.4% O₂, 300 ppm propene and 300 ppm NO a similar selectivity to N₂O was measured (31% with 18 ppm N₂O for 38% NO conversion). However, in this case most of the remaining NO was oxidised to NO₂ indicating little N₂ was formed.

These results show the presence of NO can have a marked effect on hydrocarbon conversion particularly at higher hydrocarbon concentrations. Our previous work showed the catalytic photo-oxidation of low concentrations (less than 2000 ppm) of ethane, ethene, propane and propene gave more than 95% conversion to CO₂ over periods extending to more than 50 h. But this was not the case when the concentration was 4000 ppm. Then the selectivity to CO₂ decreased to ~50%, and when this was repeated in the presence of 300 ppm NO there was no significant difference in the propene conversion (at ~3%) or the selectivity to CO₂, and a brown discolouration of the titania surface was still observed indicating no major impact of the NO on the propene photo-oxidation. This observation was in keeping with propene adsorbing strongly on

Table 2

Photocatalytic propene and NO conversions for gas mixtures containing varying amounts of each at constant flow rate and oxygen concentration. Conversion are after a period of 150 mins. Total flow rate 250 ml/min, 12% O₂ at 150 °C. Selectivities for N₂O were calculated on the basis of the fraction of N from NO converted to N₂O.

NO concentration (ppm)	Propene concentration (ppm)	NO conversion (% (ppm))	NO ₂ produced (ppm)	N ₂ O produced (ppm, selectivity (%))	C ₃ H ₆ conversion (%(ppm))
300	2000	27 (81)	0		5 (104)
300	1000	41 (123)	2		13 (131)
300	580	66 (198)	8	22 (25)	53 (307)
300	300	61 (183)	10	30 (33)	96 (288)
300	152	45 (135)	42		100 (152)
300	76	32 (96)	49		100 (76)
2000	300	12 (230)	0		62 (185)
1000	300	20 (200)	0		64 (193)
580	300	44 (255)	10	46 (36)	96 (288)
152	300	78 (119)	8		100 (300)
76	300	96 (73)	0		92 (276)
152	152	59 (90)	18		100 (152)
580	580	40 (233)	10		40 (233)
1000	1000	25 (248)	0		23 (226)
2000	2000	10 (207)	6		7 (148)

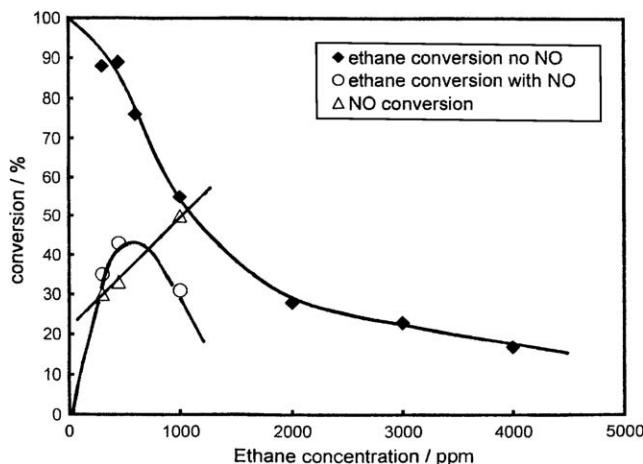


Fig. 6. Conversion of NO and ethane as a function of ethane concentration in the absence of NO and with 300 ppm NO in the gas feed.

the titania surface and preventing dioxygen and NO having access to the surface. Hydrocarbon poisoning of this type is well known in other areas such as selective NO_x reduction over silver-based catalysts [34].

3.4.2. Ethane/NO

For experiments involving both NO and C₂H₆ in the gas feed the NO and C₂H₆ conversions achieved are summarised in Fig. 6. Small amounts of NO₂ (~5 ppm) were produced with C₂H₆ concentrations of 300 ppm and 450 ppm though not when the C₂H₆ concentration was 1000 ppm. The N₂O production, was ~25 ppm, similar to that obtained with propene/NO gas feeds. The level of CO₂ indicated the conversion selectivity of C₂H₆ to CO₂ was >95% as was the case with propene. For 300 ppm propene and NO with 12% O₂ the conversions would be ~90% for propene and ~55% for the NO, therefore, both the hydrocarbon and NO conversions achieved using 300 ppm C₂H₆ in the gas feed instead of propene were significantly reduced.

With increasing C₂H₆ concentration the absolute amount of C₂H₆ converted increased, at least for C₂H₆ concentrations up to 1000 ppm. The NO conversion also increased with C₂H₆ concentration and if the C₂H₆ concentration was raised to 1000 ppm the NO conversion was slightly higher than that obtained with 1000 ppm propene. The NO conversion therefore increases with C₂H₆ concentration to 1000 ppm together with the increasing absolute ppm C₂H₆ conversion. The increased conversion of both NO and C₂H₆ with increasing gas phase concentration of C₂H₆ was presumably due to an increase in the surface coverage of either C₂H₆ or a partially reacted hydrocarbon species from its reaction with active surface oxygen. If the increased hydrocarbon coverage was not at the expense of NO the rate of reaction of NO with hydrocarbon would increase producing the observed increase in NO conversion. The increased hydrocarbon coverage would also reduce NO oxidation accounting for the elimination of NO₂ production with 1000 ppm C₂H₆. It is interesting to note that, in contrast, increasing the propene concentration from 300 ppm to 1000 ppm decreased the NO and propene conversion.

With ethane the hydrocarbon conversion was lower in the presence of NO for all the hydrocarbon concentrations measured. Ethane would be expected to interact more weakly with titania than with the alkenes propene and ethene so in this case NO may effectively compete with the hydrocarbon for surface adsorption and so reduce hydrocarbon conversion, while conferring no benefit because the surface did not acquire a carbonaceous deposit.

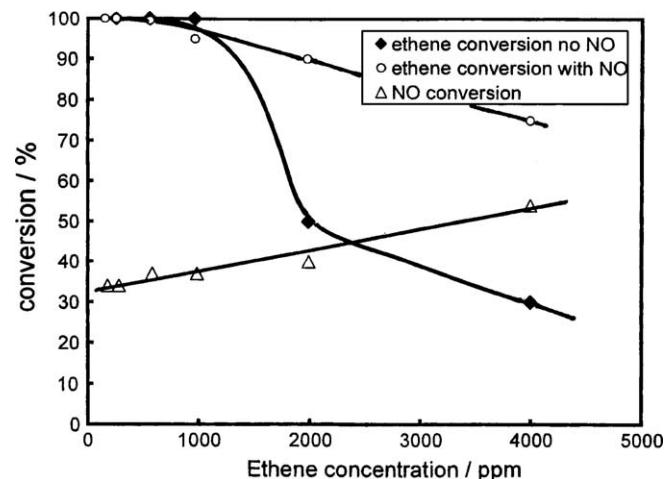


Fig. 7. Photoconversion of ethene with and without 300 ppm NO as a function of ethene concentration in the gas feed over Hombifine N TiO₂ with 12% O₂ at a flow rate of 250 ml/min at 150 °C.

3.4.3. Ethene/NO

The ethene conversion in the absence of NO (Fig. 7) levelled out above 1000 ppm, behaviour broadly similar to that of ethane except the absolute (ppm) conversion for ethene is higher than ethane, possibly reflecting a higher surface coverage of ethene. No inhibition was observed at higher hydrocarbon coverages as was the case with propene and propane. The NO conversion with ethene increased with increasing hydrocarbon concentration. The increase in NO conversion with the increasing absolute (ppm) amount of hydrocarbon converted was in common with the other hydrocarbon/NO systems we studied. In the case of 2000 and 4000 ppm ethene the presence of 300 ppm NO led to an increase in the ethene conversion from 30% to 75% at 4000 ppm, together with an increase in the selectivity to CO₂ from 54% to 76%. Likewise at 2000 ppm ethene the conversion increased from 50% to 90% with the addition of 300 ppm NO.

3.4.4. Butane/NO

As in the absence of NO *n*-butane conversions with 300 ppm NO, 12% O₂ at 150 °C were 100% up to 200 ppm *n*-butane, with 400 ppm *n*-butane the conversion fell slightly to 93%. The selectivity to CO₂ was 100% in all cases and N₂ selectivities were calculated assuming it was the only other nitrogen containing product apart from NO₂ and N₂O. These results are summarised in Table 3. The NO conversion increased with *n*-butane concentration, Table 3. With 30 ppm *n*-butane and 300 ppm NO the NO conversion was similar to that obtained for 300 ppm propene in place of butane, and slightly lower than the 69% produced by 300 ppm propane. However, with 300 ppm of both propene and propane essentially no NO₂ was. With butane concentrations in excess of 100 ppm NO₂ production was eliminated. Some N₂O (27–40 ppm) was also produced from NO/*n*-butane ion though the amount was not noticeably dependent on *n*-butane concentration in the range 30–400 ppm.

The NO conversion for ethane, ethene and propene followed the absolute amount of hydrocarbon converted indicating the two are related. A likely explanation is that partially oxidised hydrocarbon species are involved in NO conversion. This trend and the NO conversion products are discussed further in the following sections.

3.5. The nitrogen containing products

Fig. 8 shows the percentage NO conversion in reactions with hydrocarbon (300 ppm) and NO (300 ppm) for ethene, ethane,

Table 3

Summary of results for the photoconversion of butane in the presence of NO (300 ppm) and 12% O₂ at 150 °C over Hombifine N TiO₂, 250 ml/min total flow rate. Selectivities were calculated on the basis of the fraction of NO converted. N₂ selectivities were calculated assuming it was the only other nitrogen containing product apart from NO₂ and N₂O.

Butane concentration (ppm)	Butane conversion (%)	Calculated N ₂ selectivity (%)	N ₂ O selectivity (%)	NO ₂ selectivity (%)	NO conversion (%)
400	93	67	33	0	88
200	100	68	32	0	84
100	100	64	27	8	73
60	100	15	40	45	53
30	100	4	31	65	50

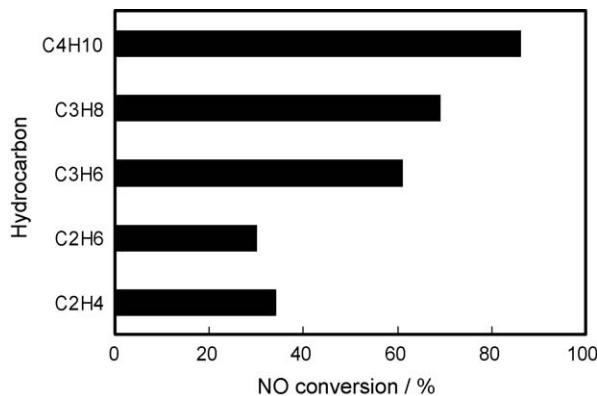


Fig. 8. NO conversion for different hydrocarbons with 300 ppm NO, 300 ppm hydrocarbon, and 12% O₂, at 150 °C, over a TiO₂ catalyst.

propene and propane. The NO conversion with *n*-butane changed only slightly with hydrocarbon concentration—88% with 400 ppm *n*-butane and slightly lower at 84% with 200 ppm *n*-butane. At 300 ppm the hydrocarbons were all oxidised to CO₂ with >90% selectivity and the hydrocarbon conversions were all >80%, but the NO conversions varied considerably. Ethene and ethane produced similar NO conversions, as did propene/propane though they were higher than ethene/ethane, *n*-butane produced the highest NO conversion. The NO conversion is therefore, to a first approximation, proportional to the hydrocarbon chain length.

The measured selectivities to N₂O and NO₂ are shown in Table 4. In the absence of HC, the vast majority of the NO was converted into NO₂, which is consistent with the absence of a reductant species. Interestingly, as the HC chain length increases above 2 (i.e. for propene, propane and *n*-butane), the presence of HC significantly promotes NO conversion. In the presence of HC

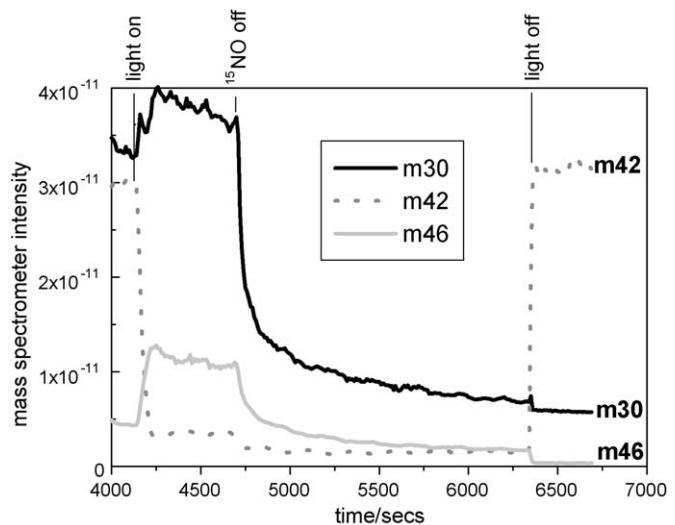


Fig. 9. Mass spectrometer traces showing mass 30 (¹⁵N₂), 42 (C₃H₆) and 46 (¹⁵N₂O). Gas feed; 300 ppm propene, 1000 ppm ¹⁵NO, 12% O₂ balance He. 150 °C, 250 ml/min total flow rate. Catalyst: Hombifine N TiO₂.

nitrogen mass balance calculations indicated there was another reaction product other than NO₂ and N₂O suggesting N₂ was produced. The derived N₂ selectivity, calculated assuming it was the only other nitrogen containing product, is also given in Table 4. The NO₂ selectivity was low though significant amounts of N₂O and N₂ were produced, selectivities for different hydrocarbons, with a constant 300 ppm NO concentration, being very similar. In these experiments the photoreaction was run for several hours to ensure conditions had stabilised and to check for gradual NO₂ breakthrough. Generally though, in the presence of propene the NO₂ stabilised much more quickly than in the absence of propene presumably due to propene adsorption reducing the number of sites for NO₂ adsorption.

To obtain more mechanistic understanding of the reaction between NO and propene and in particular to establish the nitrogen containing products, experiments were carried out using a gas feed consisting of propene/¹⁵NO/O₂/He. A typical mass spectrometer trace obtained is shown in Fig. 9. Prior to this experiment the catalyst was 'aged' by running the photocatalytic decomposition of 300 ppm propene in 12% O₂/He for 2 h at 150 °C.

Several important points were obtained from these experiments. First, it is clear from Fig. 9 a significant amount of ¹⁵N₂O (mass 46) was generated photocatalytically from ¹⁵NO/propene and O₂. Second, ¹⁵N₂ (mass 30) was produced on illumination. The formation of ¹⁵N₂ and ¹⁵N₂O could both be accounted for by the photocatalytic dissociation of ¹⁵NO followed by reaction of dissociated ¹⁵N atoms with either ¹⁵NO or other ¹⁵N atoms, though it is not clear if this is the actual mechanism. Third, small amounts (~10 ppm) of ¹⁵NO₂ (mass 47) were also observed in these experiments, consistent with the results shown in Table 2. Similar experiments using only ¹⁵NO/O₂/He mixtures with no hydrocarbon indicated the production of both ¹⁵N₂O and ¹⁵NO₂, but showed no evidence of ¹⁵N₂ formation. The presence of the hydrocarbon is necessary for N₂ formation.

4. Conclusions

In the presence of excess oxygen the photoactivated reaction of NO and propene over titania produced CO₂, NO₂, N₂O and N₂. The selectivity to the various nitrogen containing products depended on temperature and the hydrocarbon and NO concentrations. At low temperature (21–43 °C) in the presence of hydrocarbon and in the absence of hydrocarbon NO conversion to NO₂ predominated,

Table 4

NO conversions and N product selectivities for photoinduced reaction of 300 ppm NO in the absence and presence of 300 ppm of different hydrocarbons, with 12% O₂ over titania at 150 °C. The cited selectivities are based on the fraction of NO converted. N₂ selectivities were calculated assuming it was the only other nitrogen containing product apart from NO₂ and N₂O.

Hydrocarbon	Calculated N ₂ selectivity (%)	N ₂ O selectivity (%)	NO ₂ selectivity (%)	NO conversion (%)
None	0	~92 ^a	29	
Ethene	60	35	5	34
Ethane	47	47	6	30
Propene	62	33	5	61
Propane	69	31	0	69
<i>n</i> -Butane (400 ppm)	67	33	0	88

^a NO₂ very slow to stabilise, ~3 h.

but at 150 °C and in the presence of hydrocarbon N₂O and N₂ were also formed. NO conversion generally increased with an increasing absolute (ppm) amount of hydrocarbon converted. Similar trends were obtained with ethane, ethene, propane and *n*-butane and there was an increase in NO conversion with increasing hydrocarbon chain length at 300 ppm NO and 300 ppm hydrocarbon. These results indicate that photoactivated hydrocarbon species are responsible for the reduction of NO at 150 °C.

References

- [1] C.T. Brigden, S. Poulston, M.V. Twigg, A.P. Walker, A.J.J. Wilkins, *Appl. Catal. B* 32 (2001) 63.
- [2] N. Negishi, K. Takeuchi, *J. Sol-Gel Sci. Technol.* 22 (2001) 23.
- [3] Th. Maggos, J.G. Bartzis, M. Liakou and C. Gobin, *J. Hazard. Mater.*, in press.
- [4] H. Wang, Z. Wu, W. Zhao, B. Guan, *Chemosphere* 66 (2007) 185.
- [5] F. Toma, G. Bertrand, S.O. Chwa, C. Meunier, D. Klein, C. Coddet, *Surf. Coat. Technol.* 200 (2006) 5855.
- [6] C.H. Ao, S.C. Lee, S.C. Zou, C.L. Mak, *Appl. Catal. B: Environ.* 49 (2004) 187.
- [7] J.S. Dalton, P.A. Janes, N.G. Jones, J.A. Nicholson, K.R. Hallam, G.C. Allen, *Environ. Pollut.* 146 (2007) 668.
- [8] S. Matsuda, H. Hatano, A. Tsutsumi, *Chem. Eng. J.* 82 (2001) 183.
- [9] S. Devahastin, C. Fan, K. Li, D.H. Chen, *J. Photochem. Photobiol. A* 156 (2003) 161.
- [10] H. Ichiura, T. Kitaoka, H. Tanaka, *Chemosphere* 9 (2003) 855.
- [11] K. Hashimoto, K. Wasada, N. Toukai, H. Kominami, Y. Kera, *J. Photochem. Photobiol. A-Chem.* 136 (2000) 103.
- [12] N. Negishi, K. Takeuchi, T. Ibuski, *J. Meter. Sci.* 33 (1998) 5789.
- [13] J. Zhang, T. Ayusawa, M. Minagawa, K. inugawa, H. Yamashita, M. Matsuoka, M. Anpo, *J. Catal.* 198 (2001) 1.
- [14] H. Courbon, P. Pichat, *J. Chem. Soc., Faraday Trans. 1* (80) (1984) 3175.
- [15] C.N. Rusu, J.T. Yates Jr., *J. Phys. Chem. B* 104 (2000) 1729.
- [16] N. Bredemeyer, S. de Buhr, D. Hesse, *Chem. Eng. Technol.* 23 (2000) 527.
- [17] J.C.S. Wu, Y.T. Cheng, *J. Catal.* 237 (2006) 393.
- [18] J.H. Thomas, in: C.F.H. Tiffer (Ed.), *Oxidation and Combustion Reviews*, vol.1, Elsevier, Amsterdam, 1965, p. 137.
- [19] M.V. Twigg, *Chem. Eng.* (March, 2007) 28.
- [20] A. Ueda, K. Ejima, M. Azuma, T. Kobayashi, *Catal. Lett.* 53 (1998) 73.
- [21] C.H. Ao, S.C. Lee, C.L. Mak, L.Y. Chan, *Appl. Catal. B* 42 (2003) 119.
- [22] C.H. Ao, S.C. Lee, J.C. Yu, *J. Photochem. Photobiol. A-Chem.* 156 (2003) 171.
- [23] N. Bowering, G.S. Walker, P.G. Harrison, *Appl. Catal. B* 62 (2006) 208.
- [24] T. Tanaka, K. Teramura, K. Arakaki, T. Funabiki, *Chem. Commun.* (2002) 2742.
- [25] R. Burch, J.P. Breen, F.C. Meunier, *Appl. Catal. B* 39 (2002) 283.
- [26] R. Mital, S.C. Huang, B.J. Stroia, R.C. Yu, *SAE paper 2002-01-0956*. (2002).
- [27] N.W. Cant, I.O.Y. Liu, *Catal. Today* 63 (2000) 133.
- [28] H. Akama, K. Matsushita, *Catal. Surveys Japan* 3 (1999) 139.
- [29] V.I. Parvulescu, P. Grange, B. Delmon, *Catal. Today* 46 (1998) 233.
- [30] A.P. Walker, *Catal. Today* 26 (1995) 107.
- [31] Further details are given in: C.J. Bradwell, Studies of the thermal stability of barium nitrate and the photochemical oxidation of propene, M Phil Thesis, University of Bradford, 2004, pp. 52–57.; P.C. Hind, Photo-induced processes at gas-solid interfaces, PhD Thesis, University of Bradford, 2006, pp. 88–92.
- [32] C. Hägglund, B. Kasemo, L. Österlund, *J. Phys. Chem. B* 109 (2005) 10886.
- [33] S. Preis, A. Kachina, N.C. Santiago, J. Kallas, *Catal. Today* 101 (2005) 353.
- [34] V. Houel, P. Millington, S. Pollington, S. Poulston, R.R. Rajaram, A. Tsolakis, *Catal. Today* 114 (2006) 334.